Removal of quaternary ammonium compounds in ion exchange process

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Abstract. The study attempted to evaluate the effectiveness of ion exchange process in cationic surfactant (benzalkonium chloride, BAC) removal from model solutions. Four commercial cation-exchange resins were chosen for the batch tests in four doses (2.5–20 mL L⁻¹). The experiments included evaluation of the following parameters on ion exchange efficiency: resin characteristics and dose, presence of inorganic salt and pH of treated solution. The ion exchange process was found to be very effective in cationic surfactant removal – two of tested resins allowed to remove up to 80% of contaminant after contact time of 40 minutes, the last two – after 60 minutes of mixing in all range of doses. The presence of electrolyte neither pH change has no essential effect on surfactant removal efficiency. The analysis of the ion exchange isotherms showed that the strongly-acidic macroporous resin C150 H was characterized by the highest BAC ion exchange capacity (153.8 mg mL⁻¹), while the weakly-acidic gel resin C104 showed the best affinity of the exchanged ions to the resin matrix.

1 Introduction

In the 21st century the fresh water deficiency become a significant problem. Progressive urban and industrial development leads to large water demand. In order to conserve the water resources, most countries implement recycling and reuse of wastewater [1]. However, some anthropological contaminants like surfactants may be difficult to remove from wastewater in conventional methods.

Surfactants are a group of organic compounds consisting of hydrophilic heads and hydrophobic tails. They have been widely used as detergents, wetting agents, emulsifiers, foaming agents as well as dispersants [2]. Depending on hydrophilic part dissociating ion, surfactants are classified into four groups: anionic, cationic, non-ionic and zwitterionic. Quaternary ammonium salts such as benzalkonium chloride (BAC) are the major and most abundant contributing cationic surfactant constituents. BAC is commonly used as biocide, preservative, pesticide, antifungal agent due to its destructive action versus cells [3]. Due to the diversity of surfactants and their physico-chemical properties it is difficult to develop a single and an effective treatment method of surfactant-contaminated wastewater. Literature data survey evidence that such processes as biodegradation, coagulation, foaming,

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photocatalytic oxidation and membrane technology [4–9] may found application in surfactants removal. Moreover, many research involving surfactants removal is focused on adsorption methods with the use of such adsorbents as activated carbon, carbon nanotubes, clays, sand, minerals (zeolite, akageneite) or ashes [10–16]. Taking into account the ionic character of surfactants, it was found that the ion exchange process may be a suitable method for surfactants removal [17], moreover ion exchange resins may be more effective in surfactants removal than conventional adsorbents. Schuricht et al. [17] compared removal efficiency of perfluorinated surfactants from wastewater by adsorption on activated carbon and ion exchange with the use of anion exchange resins. The ion exchange and hydrophobic interaction were found to be involved in the sorption processes on resins, while for activated carbon, surfactant removal is only due to physisorptively bound to activated carbons. Schouten et al. [18] reported anion exchanger IRA-900 capacity versus anionic surfactant linear alkyl benzene sulfonate (LAS) equal to 3.7 mmol LAS/g dry resin which is relatively high and close to the specified ion exchange capacity of 4.2 meq/g dry resin.

2 Experimental

Quaternary ammonium compound, benzalkonium chloride (BAC) was subject of the tests (Table 1). Model solutions containing 50, 100 and 250 mg BAC L⁻¹ were prepared from distilled water and benzalkonium chloride (BAC). The concentration of surfactant was determined using spectroscopic measurements (UV Mini 1240 spectrophotometer, Shimadzu). In order to verify the effect of electrolyte on the process efficiency, sodium chloride (NaCl, Poch, Poland) was added to prepared solutions. pH correction was achieved by adding 0.1 M HCl and 0.1 M NaOH solutions to prepared feeds. pH value of BAC solutions without any correction amounted to 6.8-7.1. HQ11D pH meter, Hach was employed for pH analysis.

Table 1. Characteristics of benzalkonium chloride.

Name	BAC (benzalkonium chloride)
Type	cationic
Chemical structure	n=8,10,12,14,16,18
Molecular weight, Da	283.80–423.97
Carbon atoms in chain	8–18
CMC, g L ⁻¹	350±5 at 22°C
Monomer length, nm	5.9 ± 0.5
Purity	80%

Four cation exchange resins which characteristics is presented in Table 2 were used in the experiments. Brand new resins C150H, Dowex 88 and Marathon 1200 were regenerated with the use of 12% NaCl solution and soaked in distilled water until regeneration agent vanished. A weakly-acidic C104 plus resin were applied in hydrogen form. The ion exchange process was carried out in 2 L reactors containing 1 L of the solution and charged with resin doses of 2.5, 5, 10 and 20 mL. The reactors were placed on Velp Scientifica FC6S flocculator and stirred at the rotational speed of 150 rpm, which ensured the uniform distribution of the resin within the entire volume of the solution. Samples were collected for BAC concentration measurement after pre-defined mixing periods (5–120 min).

Table 2. Characteristics of cation exchange resins

Resin	Type	Structure	Functional group	Grain size, μm	Exchange capacity*, eq L^{-1}
C150 H	strong acidic	polystyrene crosslinked with divinylbenzene, macroporous	sulfonate	600–850	1.7
Dowex 88	strong acidic	styrene-DVB, macroporous	sulfonate	300–1200	1.8
Marathon 1200 Na	strong acidic	styrene-divinylbenzene, gel	sulfonate	535–635	≥ 2.0
C104 plus	weak acidic	crosslinked polyacrylic acid, gel	carboxylic	300–1200	4.2

* producer data

Ion exchange isotherms can be described by numerous mathematical models. In this paper, the classical approach of the linear-form of Langmuir model was analyzed:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{1}$$

where: q_e (mg mL^{-1}) – equilibrium amount of BAC exchanged on a resin volume of 1 mL calculated from the following equation:

$$q_e = (C_i - C_e) \frac{V}{V_J} \tag{2}$$

where: C_i (mg L^{-1}) – initial BAC concentration, C_e (mg L^{-1}) – equilibrium BAC concentration, V (L) – solution volume, V_J (mL) – resin volume, q_{max} (mg mL^{-1}) – maximum uptake of BAC exchanged on a resin volume of 1 mL, K_L (L mg^{-1}) – Langmuir constant.

The efficiency of BAC removal was calculated from following formula:

$$R = \frac{(C_i - C_e)}{C_i} \cdot 100, \% \tag{3}$$

3 Results and discussion

Figures 1 and 2 present kinetic profiles obtained in the 120 min experiments. Similar course of curves was noted for all resins – increasing mixing time and resin dose resulted in BAC removal enhancement. It should be noted that in the first stage of the processes (up to 20 min), the intensity of the ion exchange was the most dynamic. With the increase of mixing time, the kinetics of the ion exchange slowed down and the equilibrium state was achieved. Strongly-acidic resins C150 H and Marathon 1200 Na established equilibrium after mixing time of 40 minutes (resin dose of 5, 10 and 20 mL, initial BAC concentration of 50 mg L^{-1}). Weakly-acidic resin C104 plus required longer contact time. It was also noted that increasing resin dose brought an improvement in BAC removal, ex. the increase of Marathon 1200 Na

dose in the range from 2.5 to 20 mL improved the removal efficiency from 50 to 100% for 20 min of mixing.

For all tested adsorbents in the dose of 2.5 mL, it can be observed that equilibrium established after more than 60 minutes of mixing (C150 H, Marathon 1200 Na) or even did not steadied during 120 minutes experiment (Dowex 88, C104 plus). The same phenomenon occurred when initial surfactant concentration increased. It may be deduced that with the decreasing of resin dose and increasing of the number of ions for exchange (BAC concentration), the process driving force rises. When the number of macroions per volume of resin increases, the potential difference between resin phase and solution phase grows. As a result, the larger number of BAC ions was attracted to the surface of the resin. Moreover, with the smaller volume of resin (per unit of surfactant volume), the competition between BAC molecules for active places occupation rise, thus establishing equilibrium state takes a longer time.

Fig. 1. The effect of contact time and ion-exchange resin dose on the efficiency of BAC removal from solution of initial concentration 50 mg L^{-1} .

In order to verify the effect of pH on BAC removal in the ion exchange process, two resins (macroporous strongly-acidic and gel weakly-acidic) were applied. The initial BAC concentration amounted to 50 mg L^{-1} . The results obtained are plotted in Figure 3. It can be observed that for strongly-acidic C150 H resin, the change in pH value did not bring any significant effect on surfactant removal efficiency. Only at the lowest pH value, a slight drop in removal was seen. Analysis of weakly-acidic C104 plus resin curves shows a big drop in process efficiency at $\text{pH} = 3$ comparing to data presented in Figure 2 (after 60 minutes of mixing, 100% of BAC was removed). At $\text{pH}=3$, maximum removal did not exceed 50% after 120 minutes of mixing. Weak-acidic resins with carboxylic functional groups have pK_a values below 6 [19], as a consequence, the degree of dissociation of these resins is

strongly influenced by the solution pH – functional groups will not readily give up a proton unless the pH is greater than 6. At a pH lower than 6, weak-acidic resins have greater affinity to hydrogen and will not exchange it for another cations [20]. As a result, for low pH values, process is limited and less BAC macroions may be bounded to the active sites.

Fig. 2. The effect of contact time and BAC concentration on the efficiency of BAC removal (resin dose 5 mL).

Figure 4 presents the effect of inorganic salt (NaCl) on BAC removal for all resins analyzed in this study. It was noted that for Dowex 88 resin, the presence of electrolyte brought an essential deterioration in removal efficiency, and for the resin dose of 2.5 mL this phenomenon was more pronounced than for dose of 5 mL. For example, after mixing time of 20 min, BAC removal amounted to 39.8% and to 70.5% for resin dose of 5 and 10 mL, respectively (salt concentration of 0.5 g L^{-1}). Increasing salt content from 0.5 to 1 g L^{-1} did not affect BAC removal - retention coefficient changed from 39.8 to 37.8% and from 70.5 and 73.9% for resin dose of 5 and 10 mL, respectively.

Fig. 3. The effect of contact time and pH on the efficiency of BAC removal efficiency from solution of initial concentration 50 mg L⁻¹, resin dose 5 mL.

Fig. 4. The effect of contact time and addition of electrolyte on the efficiency of BAC removal from solution of initial concentration 50 mg L⁻¹.

Based on the linear-form of Langmuir model (equations 1 and 2) and the tangent of the slope angle of the curve $f(C_e) = C_e/q_e$ (Figure 5), the parameters q_{max} and K_L were calculated for all tested resins and compared in Table 3. Maximum exchange capacity values (q_{max} , maximum uptake of BAC exchanged on a resin volume unit) listed from the highest to the lowest amounted to 158.3, 116.3, 103.1 and 77.5 mg mL⁻¹ for C150 H, Marathon 1200 Na, Dowex 88 and C104 plus resins, respectively. In accordance to the previous part of the study, the strongly-acidic macroporous resin C150 H proved to be the most suitable for BAC removal against all tested resins. Gel resins, C104 plus and Marathon 1200 Na achieved worse ion exchange capacity. This is due to higher degree of polymer crosslinking

(comparing to macroporous resins) – surfactant monomers access to the active sites of gel resins is limited by the compact structure of the matrix. Due to the relatively large grain size (300–1200 μm) of macroporous resin Dowex 88, BAC macroions penetration to the resin’s active sites was restricted. As a result, this resin showed a worse capacity than the gel resin Marathon 1200 Na.

Fig. 5. The linear form of benzalkonium chloride ion exchange isotherms.

K_L (Langmuir constant) parameter is being used for evaluation the affinity of ions exchanged to the resin structural polymer. Taking into account K_L values, Dowex 88 resin showed the lowest affinity, which may explain BAC removal deterioration in the presence of inorganic salt (Figure 4). As a result of low BAC affinity to Dowex 88 resin, other ions (e.g. Na^+) are being exchanged preferentially limiting at the same time BAC removal. C104 plus resin achieved the highest value of K_L parameter, however this weakly-acidic gel resin cannot remove such number of surfactant macroions as macroporous strongly-acidic resin due to the lower pore size and the worse selectivity.

Table 3. Langmuir isotherms parameters for benzalkonium chloride ion exchange.

Parameter	C150 H	Dowex 88	Marathon 1200 Na	C104 plus
$q_{max}, \text{mg mL}^{-1}$	153.8	103.1	116.3	77.5
$K_L, \text{L mg}^{-1}$	0.478	0.055	0.424	0.603

4 Summary

- The research conducted proved the ion exchange process is an effective method for benzalkonium chloride removal from water. The process efficiency enhanced with extending mixing time and increasing resin dose.
- The change in pH value of the treated solution has no significant effect on surfactant removal with the use of strongly-acidic resin. Weak-acidic resin which degree of the functional groups’ dissociation is dependent on solution pH, showed decrease in BAC removal at low pH value.
- The resin matrix (gel or macroporous) and the grain size affect the macroions access to the active sites, thus – on the ion exchange efficiency.

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